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AND

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Effect of Storing Cement in the Atmosphere.

THE effect of atmospheric storage on two ordinary and two high-strength Portland cements is discussed by V. M. Anzlov in *Zement*. The properties of the cements stored in sealed tins were practically unchanged after one year. The cements stored in jute sacks suffered important changes. Setting time increased with time of storage, the ordinary cements being less affected than the high-strength cements. The setting time of ordinary Portland after seven days' storage was three hours thirty minutes initial and five hours twenty-five minutes final; after twelve months' storage the initial setting time was five hours thirty minutes and the final ten hours twenty minutes. High-strength cement after seven days' storage had an initial setting time of forty-five minutes and a final setting time of two hours; after twelve months' storage the initial setting time was five hours twenty minutes and the final setting time seven hours fifteen minutes. In general the residue on the 180 sieve was reduced by twelve months' storage, although some lumping occurred. The water required for normal consistency increased with time of storage (e.g., from 27 to 29.5 per cent. in one year), and the Le Chatelier expansion decreased (e.g., from 2.5 mm. to zero). Loss on ignition increased (e.g., 1.1 to 10.25 per cent. in one year) and specific gravity diminished (e.g., 3.10 to 2.84).

Atmospheric storage caused a continuous fall of tensile and crushing strength; this is more evident in the crushing strength figures, which are a more reliable criterion of strength than tensile figures. It may be mentioned that the values obtained with neat cement gave inconsistent results, whereas the values for 1:3 mortar were consistent; it is the latter that are referred to in the following. The strength values of test-pieces of 1:3 mortar made with cement stored in jute sacks for one year are expressed as a percentage of those for cement stored seven days, and only crushing strengths are here considered. Ordinary Portland cement test-pieces stored for one day in moist air, two days in water, and in the atmosphere for the remainder of the period had a strength at one year of 46.1 per cent. of the 7-day strength; in the case of test-pieces stored in moist air for

one day and twenty-seven days in water, the one-year strength was 83.6 per cent. of the 7-day strength. High-strength Portland cement test-pieces, stored one day in moist air, two days in water, and in the atmosphere for the remainder of the period had at the age of one year a strength 30.5 per cent. of the 7-day strength; similar test-pieces stored for one day in moist air, twenty-seven days in water, and in the atmosphere for the remainder of the period had a strength 65.3 per cent. of the 7-day strength.

Cement test-pieces stored for one day in moist air and two days in water had the following percentage strengths: cement stored seven days, strength 100; one year, strength 46.1; test-pieces stored for one day in moist air and twenty-seven days in water cement stored seven days, strength 100; cement stored one year, strength 83.6. High-strength Portland, test-pieces stored one day moist air, two days water: cement stored seven days, strength 100; one year, strength 30.5; test-pieces stored one day moist air, twenty-seven days water: cement stored one year, strength 65.3 per cent. of strength of cement stored for seven days.

The fall in strength is thus greater with the high-strength than with the ordinary cements. It is also greater for the short-date than for the long-date tests, i.e., the high-strength cements lose their characteristic property of high initial strength on prolonged exposure to the atmosphere.

Book Review.

"La Chimica del Cemento. Part I. Il Cemento Portland." By Quirino Sestini. Pp. 228. (Milan: Ulrico Hoepli. Price 28 lire.)—This is a useful review in the Italian language of world-wide publications on the chemistry of Portland cement. Except for the work of Vicat, of which some account is given, the literature of cement chemistry does not begin before the end of the last century, when Le Chatelier published his ideas of the silicates and aluminates of lime present in cement, Toinebohm suggested the terms alite, belite, celite, and felite for the mineralogical constituents of cement clinker, and Michaelis enunciated the gel theory of setting. With the opening of the present century the efforts of chemists to throw light on the constitution of cement and the changes that occurred during setting became widespread, and the book refers to the subject of solid solutions introduced by Clifford Richardson. Subsequent chapters deal with the thermo-chemistry of cement when the names of Nacken and Hendrickx appear, and the subject of chemical equilibria and binary and ternary diagrams when the American observers Shepherd, Wright, Rankin, and Day become prominent. The summary is then brought up to date by a description of the work of Lerch, Bogue, Kuhl, Guttman, Gille, and others. Separate chapters are devoted to X-ray research and the evaluation of cement by chemical analysis and by microscope sections, the latter being suitably illustrated.

The chemistry of the setting and hardening, including "false" set, is adequately summarised, and includes the recent work of Dörsch and Forsen. The numerous references to the sources of information from which the book is compiled do not always include the original papers of the authors referred to, but apart from this the book can be recommended to those wishing to follow the development of cement chemistry and to learn the present theories that are held. A second volume dealing with rapid hardening cements is promised.

Rotary Kiln Exit Gases—Some Relationships.

By W. T. HOWE

CHIEF CHEMIST, G. AND T. EARLE, LTD.

THE study of rotary kiln heat problems is connected very largely with the composition of the exit gases, and a thorough understanding of the principles involved is necessary. This article is an attempt to describe some of the factors concerned and to discuss their effects. Gas analysis control has been carried out for a number of years at some cement works, and when used with intelligence has proved to be really valuable.

To commence with the simplest case, consider a kiln which uses pure carbon as fuel to burn raw material which on heating evolves only carbon dioxide from the calcium carbonate present. The CO_2 evolved from the combustion of 1 lb. of carbon will be $44 \div 12$ lb., while 44 lb. of CO_2 are produced from 100 lb. of calcium carbonate. Also, 1 lb. of carbon requires $32 \div 12$ lb. of oxygen for its combustion, which needs $\frac{32}{12} \times \frac{100}{23}$ lb. of air, and consequently $\frac{32}{12} \times \frac{77}{23}$ lb. of nitrogen remain after combustion, and will appear in the exit gases mixed with the CO_2 . Now, assume that N lb. of carbon is required to produce 100 lb. of clinker, and the CaCO_3 in the raw material is l per cent.

$$\text{Then, } \text{CO}_2 \text{ from combustion} = \frac{44}{12} N \text{ lb. per 100 lb. of clinker.}$$

$$\text{CO}_2 \text{ „ raw materials} = 0.44l \text{ „ „ „}$$

$$\text{N}_2 \text{ „ combustion} = \frac{32}{12} \times \frac{77}{23} N \text{ „ „ „}$$

We are assuming that combustion is perfect, with no excess air. We can find the volume relationship by analysing the exit gases with an Orsat apparatus, from which we obtain the percentage by volume of CO_2 , and, as other gases are absent, the residual gas will be nitrogen. Suppose that a per cent. of CO_2 is found. Then $100 - a$ per cent. of N_2 is also present. The densities of CO_2 and N_2 are 22 and 14 respectively, consequently the relative proportions of CO_2 and N_2 by weight will be $22a : 14(100 - a)$. But we know the weights present from our original suppositions, and consequently we may form the following equation:

$$\frac{22a}{14(100 - a)} = \frac{\frac{44}{12} N + 0.44l}{\frac{32}{12} \times \frac{77}{23} N} \quad \dots \dots \dots (1)$$

By reduction and transposition,

$$N = \frac{l(100 - a)}{40(a - 21)} \text{ and } a = \frac{100(l + 8.4N)}{l + 40N}$$

where N = pounds of carbon burnt per 100 lb. of clinker made.

a = percentage of CO_2 in kiln exit-gases by volume.

l = „ „ CaCO_3 in raw materials.

This is the simplest relationship between these factors, but in practice there are considerable modifications due to various causes. Coal is never pure carbon,

and contains other elements which affect the gas analysis, as the hydrogen present requires oxygen to form water, which is not estimated, but the oxygen used leaves nitrogen which alters the ratio of CO_2 to N_2 . Other factors disturbing to a minor degree are the sulphur, oxygen and nitrogen present in the coal. Most cement raw materials contain organic matter which burns, requiring air and adding its quota of CO_2 and N_2 to the exit gases, whilst they also contain small quantities of magnesium carbonate as well as sulphur compounds. Also, combustion is never perfect and the gases contain varying amounts of excess air, often with certain reducing gases. These factors all affect the problem in varying degrees, and the following is an attempt to show their effects and relationships.

The exit gases from a cement rotary kiln may be considered to be composed of the following constituents: (1) Gases from combustion of fuel, (2) excess air above that required for perfect combustion, (3) water vapour from evaporation of water in slurry, (4) carbon dioxide from decomposition of carbonates in raw materials, (5) gases derived from combustion of organic matter in the raw materials.

In addition there will be small quantities of other gases, etc., such as water vapour due to atmospheric humidity, gaseous sulphur compounds from sulphur in raw materials, hydro-carbons, ammonia, etc., from imperfect combustion of coal, etc.

The usual method of gas analysis, with Orsat or similar apparatus, consists essentially in absorbing the acid gases, such as carbon dioxide, sulphur dioxide and sulphuretted hydrogen, when present, in an alkaline solution, the result being reported as "carbon dioxide"; this is followed by absorption of oxygen, usually by alkaline pyrogallate or possibly phosphorus, then absorbing carbon monoxide by means of a solution of suitably prepared cuprous chloride. The balance of gas remaining is reported as nitrogen. This method ignores the water vapour content of the gases, and the minor constituents will be absorbed by one or other of the solutions used, without, in usual cases, causing any serious error, the values being within the possible errors of the method used.

We can, however, use the results of the analysis, together with known information regarding the analyses of the fuel and raw materials, to obtain valuable data as to the running of the kilns with special regard to kiln efficiency. Some of the relationships are discussed in the following.

Kiln Coal Consumption from Gas Analysis.

The results of the gas analysis may be re-cast to show (a) total CO_2 , etc., (b) CO due to incomplete combustion, (c) excess air, and (d) nitrogen remaining after allowing for that contained in excess air. The CO_2 includes that derived from combustion of fuel and that derived from the raw material, either by dissociation of carbonates or combustion of organic matter in raw material. The nitrogen is derived mainly from the air used for combustion of fuel, together with that remaining from air used for combustion of organic matter in raw material. Analysis of the fuel and raw material will give the gases formed from

combustion or evolved on heating, and with this information we can calculate a formula which may be used for kiln control, etc.

In a previous article, "Rotary Kiln Heat Balance" (CEMENT AND CEMENT MANUFACTURE, May, 1933), it was shown that the weight of CO_2 produced for each 100 lb. of clinker made was

$$\frac{98.1 l}{221-l} + 0.79 m \text{ lb.}$$

where l = percentage of CaCO_3 in raw materials, and

m = " " " MgCO_3 " " "

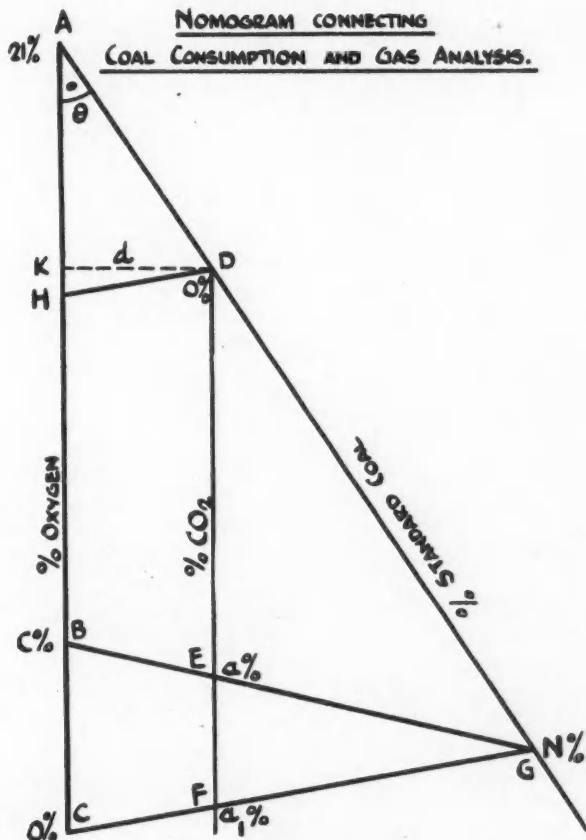


Fig. 1.

A table calculated from this equation was given, but it may be represented with sufficient accuracy by a simpler but empirical linear relationship

and, allowing for an average value of 1.5 per cent. of MgCO_3 present in British raw materials, the weight of CO_2 derived from the raw materials required for the production of 100 lb. of clinker is

$$\text{WCO}_2 = 1.032 (l-25).$$

The influence of the organic matter contained in the raw material may also be obtained from this article. It was shown in the article referred to that 1 lb. of organic matter when burnt gives 2.2 lb. of CO_2 and 6.24 lb. of nitrogen. Consequently for 100 lb. of clinker there will be, where p = percentage of organic matter, $3.5 p$ lb. of CO_2 and $10 p$ lb. of nitrogen.

The products of combustion of the coal may also be obtained from the same article. For this purpose the "ultimate" analysis of the coal will be required, although, as will be shown later, a close approximation to the final result may be obtained without its use, as the characteristics of coal depend on its group, *e.g.*, anthracite, semi-anthracite, bituminous, etc.

For purposes of comparison coal quality may be expressed in terms of "Standard Coal," which throughout this article is taken as being dry coal having a calorific value of 7,000 calories per gram, or 12,600 B.T.U. per lb. Thus, knowing the coal moisture M and the calorific value V_d (on dried coal) or V_R (on raw coal as received or used) the "Standard Coal Factor" F for the coal in question is

$$F = \frac{100 - M}{100} \times \frac{V_d}{7,000} \quad \dots \dots \dots (2a)$$

$$\text{or} \quad F = \frac{V_R}{7,000} \quad \dots \dots \dots (2b)$$

according to whether the calorific value is reported as on "dry coal" or "coal as received," and, of course, in calories.

The products of combustion of 1 lb. of standard coal may now be calculated.

Where C = % carbon	}	From ultimate analysis of coal as received, having standard coal factor = F .
H = % hydrogen		
O = % oxygen		
S = % sulphur		
N = % nitrogen		

$$\text{CO}_2 \text{ will be } \frac{1}{100} \times \frac{C}{F} \times \frac{44}{12} \text{ lb. per lb. standard coal.}$$

$$\text{SO}_2 \quad \dots \quad \frac{1}{100} \times \frac{S}{F} \times \frac{64}{32} \quad \dots \quad \dots \quad \dots$$

$$\text{N}_2 \quad \dots \quad \frac{1}{100} \times \frac{77}{23} \cdot \frac{1}{F} (2.6 C + S + 8H - O + 0.3 N)$$

If the coal consumption of the kiln = N lb. of standard coal per 100 lb. of clinker, the quantities of gases for that quantity of clinker will be the above values multiplied by N . These quantities, as well as those of the other gases evolved from the raw materials, may now be converted to volumes in cubic feet at normal temperature and pressure (N.T.P.).

1 cub. ft. CO₂ weighs 0.1234 lb. at N.T.P.

1 " " SO₂ " 0.1826 " "

1 " " N₂ " 0.07843 " "

(nitrogen being "atmospheric nitrogen.")

CO₂ from raw material = 8.37 (l-25) cub. ft. per 100 lb. clinker.

CO₂ derived from organic

matter in raw material = 28.4 p " " " "

CO₂ from combustion of coal = $0.297 \frac{CN}{F}$ " " " "

SO₂ " " " " = $0.11 \frac{SN}{F}$ " " " "

N₂ " " " " = $0.427 \times \frac{N}{F} (2.6C + S + 8H - O + 0.3N)$ "

N₂ " organic matter = 127.5 p cu. ft. per 100 lb. clinker.

The actual proportions in which these gases exist in the kiln exit gases are obtained from the Orsat apparatus analyses. Thus, supposing the results show

CO₂ by volume = a per cent.

O₂ " " = c "

N₂ " " = 100 - a - c per cent.

Air " " = 4.76 c containing 3.76 c per cent. N₂

consequently the percentage of N₂ in air-free gases = 100 - a - c - 3.76 c.

= 100 - a - 4.76 c = 4.76 (21 - c) - a per cent.

The ratio of CO₂ + SO₂ to N₂ found by analysis is equal to that which may be obtained from these calculations. Thus,

$$\frac{a}{4.76(21 - c) - a} = \frac{8.37(l-25) + 28.4p + 0.297 \frac{CN}{F} + 0.11 \frac{SN}{F}}{127.5p + 0.427 \frac{N}{F} (2.6C + S + 8H + 0.3N - O)}$$

By solving this equation for $\frac{N}{F}$ we obtain

$$\frac{N}{F} = \frac{\{8.37(l-25) + 28.4p\} \{4.76(21 - c) - a\} - 127.5ap}{0.427a(2.6C + S + 8H - O + 0.3N) - \{0.297C + 0.11S\} \{4.76(21 - c) - a\}} \quad \dots (3)$$

The ratio of CO₂ + SO₂ to N₂ in the combustion gases from coal, assuming perfect combustion with no excess air, is constant for each class, within limits. Putting r for this ratio,

$$r = \frac{0.297C + 0.11S}{0.427(2.6C + S + 8H - O + 0.3N)} = \frac{0.262C}{C + \frac{1}{3}(8H - O)} \text{ very closely.}$$

Also, as will be shown later,

$$2.6C + S + 8H - O + 0.3N = 220F (\pm 1 \text{ per cent.}) \quad \dots (4)$$

Substituting in equation (4) and reducing, we obtain

$$N = \frac{\{4.76(21 - c) - a\} (l-25 + 3.4p) - 15.2ap}{11.2[a - r\{4.76(21 - c) - a\}]} \quad \dots (5)$$

NOMOGRAM SHOWING RELATIONSHIP BETWEEN KILN
EXIT GAS ANALYSIS & "STANDARD" COAL CONSUMPTION

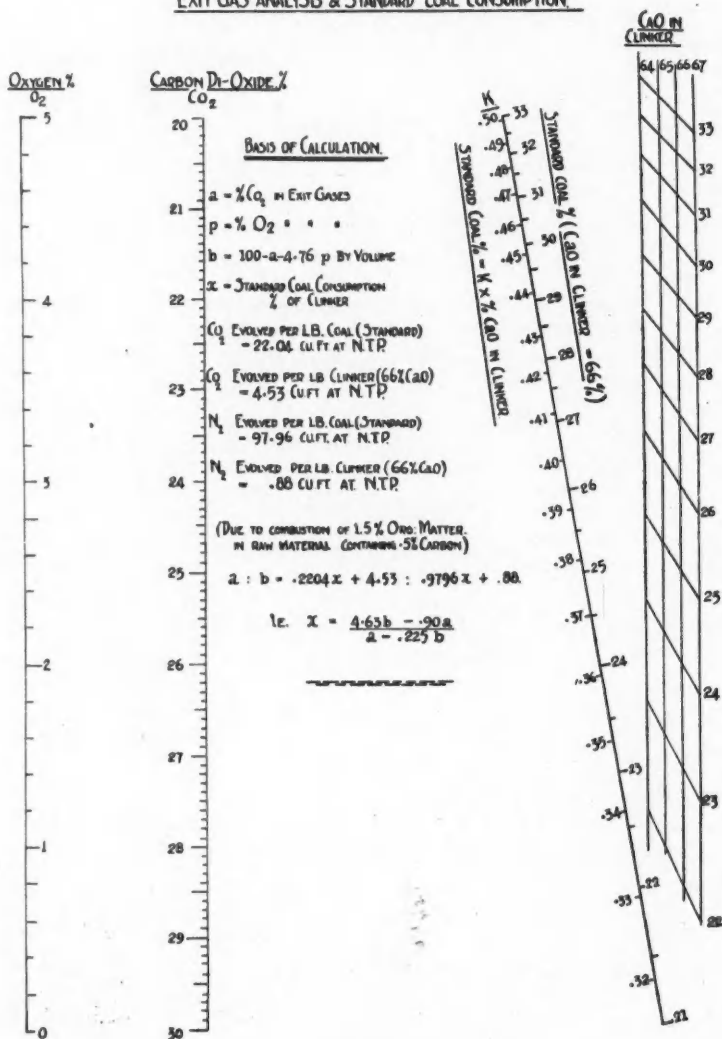


Fig. 2.

Putting $R = 4.76(21 - c)$ and re-arranging terms,

$$N = \frac{R(l-25 + 3.4p) - a(l-25 + 18.6p)}{11.2\{a(1 + r) - rR\}} \quad \dots \dots \dots (6)$$

This equation gives the percentage of standard coal from the gas analysis when the percentage of CaCO_3 and organic matter in the raw materials is known, provided the factor r is known for the coal used. This factor, however, shows considerable constancy for different classes of coal, and values will be given later thus enabling this equation to be used even in the absence of the coal ultimate analysis.

In most cement works it is usual for the CaCO_3 and organic matter in the raw material to be constant within small limits, or at any rate only two or three classes of slurry with varied CaCO_3 content are prepared for the different grades of cement produced. The average values may therefore be inserted in equation (6) to give a much simpler form. As an example, assume the $\text{CaCO}_3 = 77$ per cent. and organic matter 1 per cent. The equation would then reduce to

$$N = 6.3 \times \frac{0.785R - a}{a(1 + r) - rR} \quad \dots \dots \dots (6a)$$

Construction of Nomogram to show relation between Gas Analysis and Coal Consumption.

This equation, and the nomogram which can be prepared to fit it, will be found very useful for control purposes in works where kiln-gas analyses are carried out regularly, especially if average gas samples for each shift are taken. The result can then be compared shift by shift and the burners and management will derive much assistance from its use.

Consideration of the equation shows that for a given value of N , i.e. percentage of standard coal to clinker, the ratio $\frac{R}{a}$ is constant. If we assume perfect combustion without excess air, we should have a value for CO_2 in exit gases, denoted by a_1 , such that

$$\frac{a}{a_1} = \frac{21 - c}{21} = \frac{R}{100}, \text{ or } a = 0.01a_1R$$

For simplicity in the following treatment,

$$\begin{aligned} \text{let } k_1 &= l - 25 + 3.4p \\ k_2 &= l - 25 + 18.6p = k_1 + 15.2p \end{aligned}$$

$$\text{Then } N = \frac{k_1R - k_2a}{11.2\{a(1 + r) - rR\}} \quad \dots \dots \dots (6b)$$

Substituting for $a = 0.01a_1R$ and reducing,

$$N = \frac{100k_1 - k_2a_1}{11.2\{a_1(1 + r) - 100r\}} \quad \dots \dots \dots (7)$$

This equation enables the nomogram connecting coal consumption with CO_2 and O_2 in exit gases to be constructed. The construction is shown in Fig. 1, whilst a specimen of the nomogram used over a period of several years is shown in Fig. 2. This includes an additional scale allowing for correction for varying

percentages of CaO in clinker, this, of course, varying with the percentage of CaCO_3 in the slurry.

In Fig. 1 the "coal" line, ADG , connects the point A , representing 21 per cent. of oxygen, with D , or 0 per cent. CO_2 . Oxygen is read upwards and CO_2

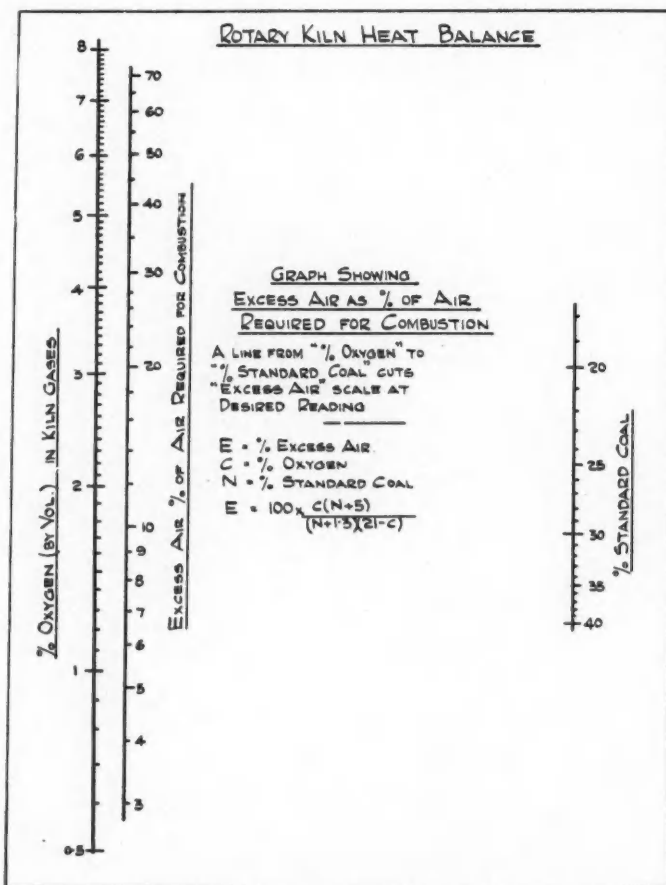


Fig. 3.

downwards, the scale of each being arranged to suit individual requirements. In the example (Fig. 2) the oxygen scale is 1 per cent. = 2 in. and the CO_2 scale is 1 per cent. = 1 in., the distance $d = 2$ in. By suitable manipulation of these scales, it is possible to bring any required range of standard coal into use.

In the diagram it can be proved from the properties of similar triangles that

$$AB : DE = AC : DF$$

By construction, $AB = 21 - c$ per cent. O_2

$$DE = a$$
 per cent. CO_2

$$AC = 21$$
 per cent. O_2

$$DF = a_1$$
 per cent. CO_2

therefore, $21 - c : a = 21 : a_1$

$$\text{or } \frac{a}{a_1} = \frac{21 - c}{21} = \frac{R}{100}$$

The point G ($= N$ per cent. standard coal) is therefore represented by a per cent. CO_2 and c per cent. oxygen or a_1 per cent. CO_2 and no oxygen.

It therefore agrees with equations (6b) and (7) and the figure is consequently an accurate nomogram for the conditions.

The calibration of the coal line must be left to the individual. However, the distance of each point from A may be calculated from the following equation representing the lengths AG , where $\frac{m}{n}$ is the scale ratio of O_2 to CO_2

$$AG = \frac{d}{\sin \theta} \times \frac{21}{21 - a_1 \times \frac{m}{n}} \quad \dots \quad (8)$$

The value of a_1 may be obtained by transposing equation (7) :

$$a_1 = \frac{100 k_1 + 1.1207N}{k_2 + 11.2N(1 + r)} \quad \dots \quad (7a)$$

As an example, if per cent. $CaCO_3 = l = 77$, per cent. organic matter $= p = 1$, $r = 0.225$.

$$a_1 = 18.37 \times \frac{N + 22}{N + 5.15} \quad [\text{from } (7a)]$$

from which the following values of a_1 may be calculated :

N .	a_1
20	30.60
22	29.70
24	28.92
26	28.23
28	27.64
30	27.11
32	26.64

In the example, Fig. 2, $m = 0.5$, and $n = 1$ where m and n are the percentages of O_2 and CO_2 per inch respectively ; $d = 2$ inches and $\sin \theta = 0.1645$.

$$\text{Therefore } AG = 12.16 \times \frac{21}{21 - \frac{a_1}{2}}$$

Where $N = 30$ per cent. standard coal, $AG = 34.3$ inches.

" $N = 22$ " " " " " $AG = 41.5$ "

Therefore the distance between $N = 22$ per cent. and $N = 30$ per cent. = 7.2 inches.

An alternative method of calibration is to calculate the values of a_1 from equation (7a) and use these values with a straightedge from 0 per cent. oxygen to mark the respective values of N . This is probably the simpler method, whilst the first method may be used as a check on a few points to ensure accuracy. To use the nomogram it is only necessary to hold the straightedge—for this purpose a strip of transparent celluloid is best—from the percentage of oxygen to the percentage of CO_2 as found in the kiln gas analysis and find where it cuts the coal line. Without a simple method of co-ordinating gas analysis with coal consumption the analytical results are often meaningless, or at least of limited value, but when the nomogram is constructed its value will soon be apparent.

Calculation of Excess Air.

In the article on "Heat Balance of Rotary Kiln," previously mentioned, the writer, under the section dealing with heat losses due to excess air, part (b), gave an equation for calculating a , i.e., the percentage of CO_2 in exit gases, from the known percentage of oxygen, c , the percentage of standard coal N . This was derived from equations 6 or (6a) in the present article by introducing average values for percentages of CaCO_3 , organic matter, and coal factor r . By transposing terms and reducing by usual algebraical methods the equation was found. The general form will be

$$a = R \times \frac{k_1 + 11.2 r N}{k_2 + 11.2 N(1 + r)} \quad \dots \dots \dots (9)$$

In the section mentioned an equation was found which expressed the percentage of excess air in terms of percentage of oxygen and percentage of CO_2 in exit gases. By introducing the value of CO_2 , or a , shown in equation (9) the following general equation was obtained expressing excess air E as percentage of total air used for combustion in terms of the percentage of oxygen in exit gases and percentage of standard coal used. This equation is valuable in cases where the gas analyses are not done regularly but an oxygen recorder is in use.

$$E = \frac{79(100 - R)}{R} \times \frac{k_2 + 11.2 N(1 + r)}{11.2(N + 1.34 p)} \quad \dots \dots \dots (10)$$

It reduces to the form given in the previous article when the appropriate works constants are introduced, thus

$$E = \frac{97c}{21 - c} \times \frac{N + 5}{N + 1.3} \quad \dots \dots \dots (10a)$$

The equation $E = \frac{376c}{4.76(21 - c) - a}$ is equivalent to

$$E = \frac{79(100 - R)}{R - a} \quad \dots \dots \dots (10b)$$

Nomograms may be constructed to suit either of the equations (10a) or (10b) and Fig. 3 shows one which is based on the former equation, allowing the percentage of excess air to be found from the percentage of oxygen in exit gases, found either by an Orsat analysis or by oxygen recorder and the coal consumption. The

construction used need not be fully described, but the basis is that the "oxygen" line is graduated proportionately to $\log \frac{c}{21-c}$, and the "coal" line to $\log \frac{N+5}{N+1.3}$. The "excess air" line is graduated proportionately to its logarithm. Scales and distances apart vary with the units taken. This nomogram is of fairly general application as wide variations in percentages of CaCO_3 , etc., make little difference to the value of E .

Correction of Standard Coal for Presence of Carbon Monoxide.

In the consideration of relations between standard coal and gas analysis the effect of carbon monoxide has so far been ignored. It must, however, be allowed for, and by means of a somewhat involved process, using the same works constants, an equation similar to (6a) has been found, but including terms for CO, represented by b :

$$N = 6.3 \times \frac{0.785R - a - 1.3b}{(a + 0.45b)(1 + r) - rR} \quad \dots \quad (6c)$$

or more generally

$$N = \frac{k_2}{11.2} \times \frac{\frac{k_1 R}{k_2} - (a + 1.3b)}{(a + 0.45b)(1 + r) - rR} \quad \dots \quad (6d)$$

thus comparing with (6a) and (6b) respectively.

It would be difficult to use these equations in practice, but fortunately the percentage of CO is usually not large and a suitable correction can be applied. Assume that the correct percentage of CO_2 to be used in equations (6a) or (6b) or the nomogram so as to give the same result as would be obtained by using equations (6c) or (6d) is a_e , the correction to be added for b per cent. of CO to the actual a per cent. of CO_2 will be

$$a_e - a = \text{approximately } \frac{b}{7} \times \frac{R + 7.5a}{0.74R - b} \quad \dots \quad (11)$$

The practical value of this correction may be taken as half the percentage of CO to be added to the percentage of CO_2 for values of CO up to 0.5 per cent., increasing slightly up to 0.6 per cent. for values of CO over 1 per cent. No practical error will be made by adding half the CO to the CO_2 unless the CO is abnormally high. In that case equation (11) may be used.

The effect of varying CaCO_3 in slurry is to increase the proportion of CO_2 from the raw material as compared with that from the combustion of the coal. An empirical correction may be applied to the nomogram result if the chart is constructed for a different value of CaCO_3 from that actually used.

If the nomogram is constructed for l per cent. CaCO_3 and the actual CaCO_3 is l_1 per cent. the value of N , or the percentage of standard coal, should be multiplied by $\frac{l_1 - l + 45}{45}$. These corrections will enable the nomogram to be used for most cases except where large variations in class of coal used are experienced. A correction for this may be applied, if required,

The series of analyses considered has been taken from the following sources :

(a) "Coal and its Scientific Uses," Bone, 1922. (b) "International Critical Tables," Vol. II. p. 131.4 and 134.11. (c) J.S.C.I., May 17, 1929, p. 105 *T* (Taylor and Patterson). (d) Fuel Research Board, National Coal Resources (Yorkshire and Lancashire). (e) "Coalfields of Yorkshire, Nottingham and Derby," 1924.

Series (a) and (b) include coals from abroad as well as this country, and (c) deals with British coals from various districts. The analyses given in (e) do not appear to have the accuracy of the others.

TABLE I.
BITUMINOUS COAL FACTORS.

No. of Analyses.	r				B/F .			
	Min.	Max.	Ave.	Average Deviation.	Min.	Max.	Ave.	Average Deviation.
(a) 9	0.2189	0.2290	0.2256	± 0.0026	216	226	221	± 2.5
(b) 3	0.2253	0.2290	0.2276	± 0.0016	220	221	220	± 0.3
(c) 8	0.2234	0.2290	0.2258	± 0.0013	220	233	225	± 3.4
(d) 39	0.2223	0.2314	0.2261	± 0.0015	212	224	217	± 1.9
(e) 10	0.2228	0.2306	0.2257	± 0.0022	209	233	220	± 7.0

From these results the values for ordinary bituminous coals may be taken as

$$r = 0.226$$

$$B/F = 220$$

These values will be at least as accurate as a single analytical result.

The values found for other classes of fuel follow, and will be useful as showing the range and also cases where these fuels may be used as admixtures.

Class of Fuel.	Series.	r .	B/F .
Peat	<i>a</i>	0.2374	203
Peat	<i>b</i>	0.2464	209
Lignite	<i>a</i>	0.2286	223
Lignite	<i>b</i>	0.2400	219
Wood	<i>b</i>	0.2534	201
Cannel Coal	<i>b</i>	0.2133	218
Coke (average of 4)	<i>b</i>	0.2561	234
Wood charcoal	<i>b</i>	0.2428	221
Semi-anthracite	<i>b</i>	0.2367	222
Anthracite	<i>b</i>	0.2402	224
" (average of 6)	<i>a</i>	0.2385	222
"	<i>c</i>	0.2363	225
Welsh steam	<i>c</i>	0.2328	220

The limiting value of r is 0.262 when the fuel consists either of pure carbon or the oxygen equals eight times the hydrogen. So far as British coals are concerned, the bituminous coals show little difference for a varying oxygen content, as the following figures indicate :

Oxygen under 6 per cent. 22 analyses. Average $r = 0.2252 \pm 0.0010$

„ $B/F = 220 \pm 2.2$

Oxygen over 6 per cent. 48 analyses. Average $r = 0.2264 \pm 0.0017$

„ $B/F = 219 \pm 3$

The variations found in studying the analyses of bituminous coals are shown in the following tables, which also show the variation in percentage of CO_2 in perfect combustion gases, this being equal to $\frac{100r}{1+r}$, and the weight of air required for 1 lb. of standard coal, which equals $B/F \div 23$.

BITUMINOUS COALS. RATIO OF CO_2 TO N_2 IN COMBUSTION GASES.

No. of Analyses.	Range of r .	% CO_2 in Perfect Combustion Gases.
1	0.2180—0.2189	17.92
10	0.2220—0.2239	18.24
26	0.2240—0.2259	18.37
17	0.2260—0.2279	18.50
13	0.2280—0.2299	18.63
2	0.2300—0.2319	18.77

BITUMINOUS COALS. RANGE OF FACTOR B/F .

No. of Analyses.	Range of B/F .	Equivalent Air. (Lb. per lb. Standard Coal).
2	209—212.9	9.18
17	213—216.9	9.35
25	217—220.9	9.52
10	221—224.9	9.70
3	225—226.9	9.83
1	229—230.9	10.00
1	233—234.0	10.15

Series (e) is not included in the latter table owing to its irregular results—possibly owing to the tests being required only for commercial purposes.

Ratio of Excess Air and Carbon Monoxide.

Perfect combustion of the fuel in the presence of sufficient air would result in gases free from carbon monoxide or other reducing gases. This condition is, however, seldom attained except perhaps when a large excess of air is present. Coal is not ground to a uniform fineness, and some particles take longer to burn than others or drop out of the gas-stream. The gases only remain above the combining temperature—or hot enough for the reaction to proceed at a fast enough rate for a few seconds; and mixing in that time is probably not perfect, so that it is rather surprising that such efficient combustion can be attained as is

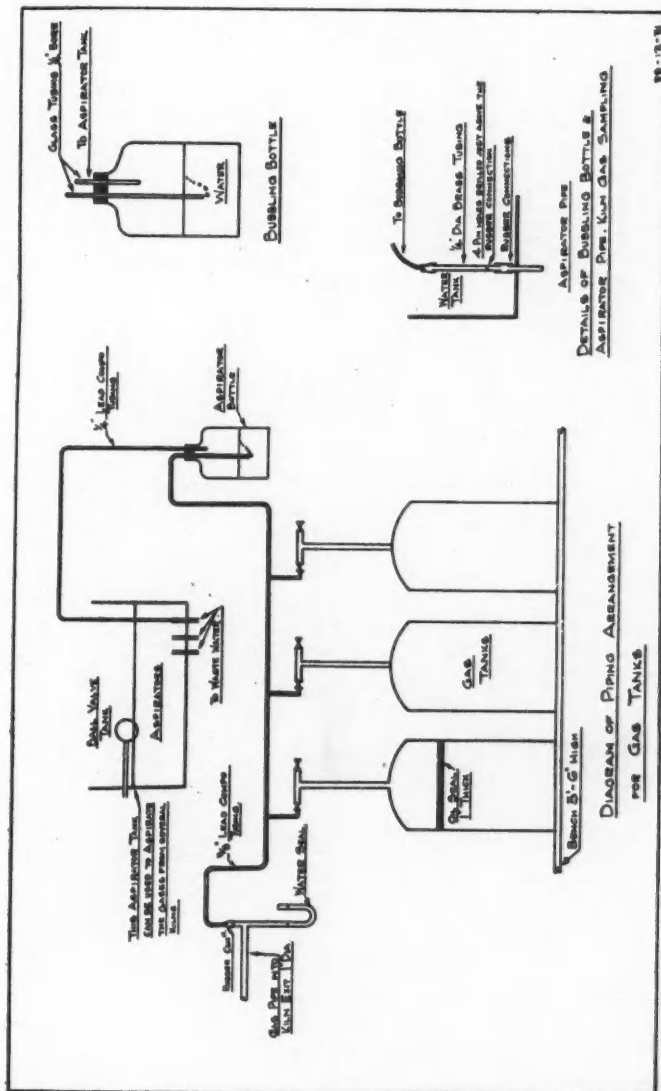


Fig. 5.

the case. It will be found, on carefully testing "snap" gas samples, that some CO is present in gases even in the presence of considerable quantities of excess air, and the graph (c) Fig. 4 shows the connection between CO and O_2 in kiln-exit gases as obtained from about 140 tests on three different kilns. Graphs (a) and (b) show the loss of heat due to the presence of CO and excess air together, in the proportions shown by (c), for (a) standard coal approximately 25 per cent. exit-gas temperature 600 deg. F., and (b) standard coal approximately 20 per cent. exit-gas temperature 400 deg. F. Both (a) and (b) show a minimum, and the

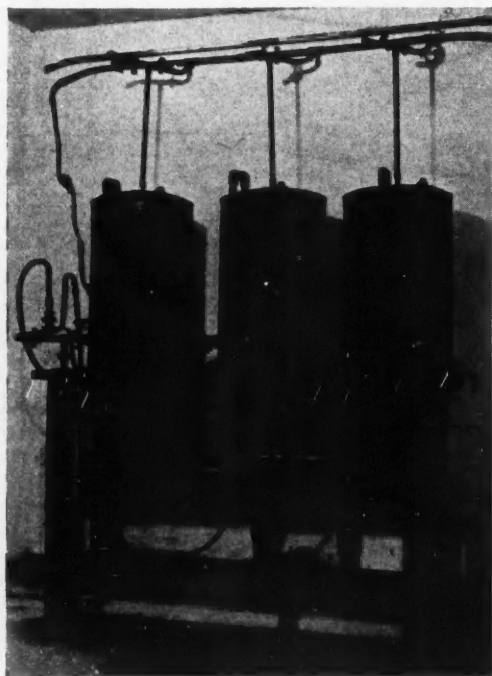


Fig. 6.

object should be to control the oxygen so that it is between the limits of 1.2 to 2.2 per cent. under conditions represented by (a), and between 1.4 to 2.4 per cent. for (b). Reference to graph (d), however, shows the necessity for some modification of these conclusions. Graph (d) shows the relation between the percentage of oxygen and the percentage of standard coal for the same series of about 140 gas analyses. The standard coal is arrived at by using the gas analyses results in connection with the nomogram connecting these factors. This graph shows a more pronounced increase of coal with higher excess air (over 1.8 per

cent. oxygen) compared with the calculated heat-loss curves *a* and *b*. This is due to the effect of gas velocity on exit-gas temperatures, there being a tendency for an increase in temperature with higher oxygen content of exit gases, and this increases the excess-air heat losses. This restricts the range of oxygen, the limits allowable in this case being approximately 1.4 to 2 per cent. The advantage of careful control of gas analysis is therefore apparent, a saving of 1 per cent. of standard coal being readily obtainable in many instances.

In this series, if the percentage of oxygen is plotted against log. CO, a straight line is obtained. This is an interesting relation, but is not confirmed in all cases. The meaning of this relationship would be that the rate of change of CO for an increment of oxygen is proportional to the CO present.

Apparatus for Gas Sampling.

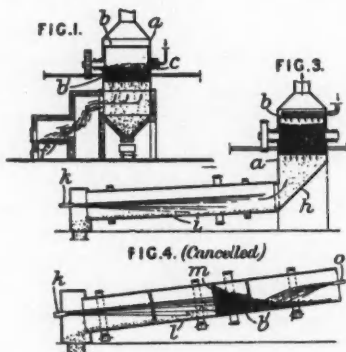
Figs. 5 and 6 show an arrangement which can be easily made and which enables an average gas sample to be taken from a kiln for any required period. The illustrations are almost self-explanatory, but it may be pointed out that the source of suction for the gas stream is the head of water in the ball-tank. Consequently alterations in this available head can be made to suit requirements. The bubbling bottle is a "tell-tale" to show whether the gas is flowing as required. Suction can be provided by a rotary blower, water, or steam ejector, or other convenient means. The oil seal in the tanks is to prevent contact between gases and water. The tanks are filled with water before commencing sampling; the water connections are not shown. The rate of sampling is governed by a drip of water from the tank. The oil seal gets saturated with the gases in time, and then acts as a bar to absorption by the water.

It will probably be found, on comparing such tank sample analyses with "snap" tests, that there is a considerably higher percentage of CO in the tank samples than would be expected from the relation between O_2 and CO shown by a series of tests as described in the preceding section. This is due to inevitable variations in burning, and the wider these fluctuations in gas analysis the higher will be the CO losses for the same average percentage of O_2 . Consequently the minimum loss position will be found to be a still higher percentage of O_2 than is to be expected from the gas analysis, and a greater saving of coal is attainable by control of gas analysis and attention to eliminating the fluctuations by a careful study of their causes. This control question is decidedly a commercial proposition. It will pay a dividend, besides leading to better results in quality and output as the kiln problems are better understood.

Recent Patents Relating to Cement.

Cements

389,976.—Mieg Muhlenbau Und Industrie Akt.-Ges., 41, Ross-strasse, Brunswick, Germany. Feb. 27, 1932.



CEMENTS.

In a process for drying, calcining, roasting, and sintering lime, cement, etc., the material is led through a perforated rotating drum containing grinding balls, etc., a stream of heating gas being directed diametrically through the drum. Fig. 1 shows one form of apparatus in which the material to be treated is fed as sludge through the hollow axle (c) of a perforated rotary drum (b) housed in a shaft (a). The drum is partly filled with loose hollow bodies (b') of metal, porcelain, etc. Gases from a furnace (f) pass up the shaft and through the drum on their way to a chimney. The treated material falls through the drum and is drawn off at the bottom of the apparatus. Fig. 3 shows an alternative

form in which the shaft (a) has a sloping bottom (h) down which the material treated in the drum (b) falls into a rotary kiln (i) where it is exposed to the action of a burner (k).

In another form the process is carried out entirely in a rotary kiln (l). The kiln has a permeable partition (m) which divides the kiln into two compartments in one of which are the hollow bodies (b'). The material to be treated is sprayed through a nozzle (o). Combustion gases from a burner (k) flow through the partition (m) while the material flows in the opposite direction and is exposed to the action of the burner (k) in the lower part of the kiln. This subject-matter does not appear in the specification as accepted.

Cements.

389,354.—Pollak, J. E., 20, Holborn, London. (Hoesch-Koln Neuessen Akt.-Ges. fur Bergbau und Huttenbetrieb; 12, Eberhardstrasse, Dortmund, Germany.) July 19th, 1932.

Iron silicate, manganese silicate, or both are added as correcting materials to cement raw materials to bring the iron or manganese oxide content in the finished clinker to between 2 and 6 per cent. The cement may thus be burned at a lower temperature than if, for example, iron oxide and quartz were used separately. Such compounds may be slags such as from the acid Martin process, from puddling furnaces, or natural silicates.

Recent Patent Applications.

396,265. Coymans, G.

Wet process for treating slurry in rotary kilns for cement.

396,964.—J. G. Farbenindustrie Akt.-Ges.

Manufacture of cement powders.

Specialities

**LOADERS
STACKERS
SCREENS
ELEVATORS
CONVEYORS
STORING & RECLAIMING PLANTS**

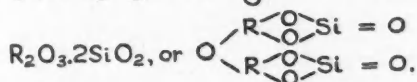
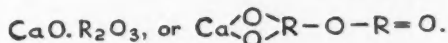
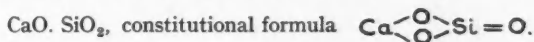


**HEPBURN
CONVEYOR CO. LTD.,
WAKEFIELD**

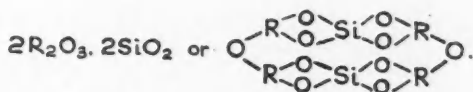
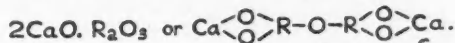
Practical Developments to be Anticipated in the Cement Industry.

By R. ZOLLINGER.

At the present day the ideal cement is believed to be represented by the formula $x \text{ 3CaO} \cdot \text{SiO}_2$, $y \text{ 2CaO} \cdot \text{R}_2\text{O}_3$. It appears pertinent to ask whether the possibilities of cement chemistry will be exhausted when this ideal cement is attained, and a study of the chemical structure of cement leads to a negative answer to this question. Interesting conclusions will be arrived at from a consideration of the structure of the important silicates, aluminates and ferrites, and of the complex compounds containing silica and the sesquioxides. The following three compounds can be taken as corresponding to the metasilicate:



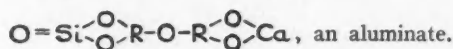
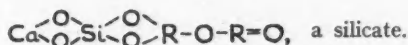
A similar parallel exists between the compounds analogous to the orthosilicates.



It is seen from these formulæ that R_2O_3 functions sometimes as a base and sometimes as an acid. This is readily explained by a closer study of the compounds formed between SiO_2 and R_2O_3 , the simplest of which is

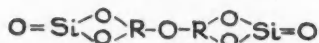


It will be seen from the constitutional formula that this compound can act as an acid in two different ways, according to the manner in which the base is combined, viz.:

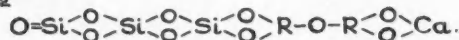
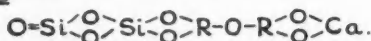
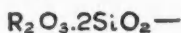


Thus the function of the R_2O_3 is entirely dependent upon how the base is combined. It must be assumed that in the raw material it is acidic and that we are there dealing with aluminates, not with silicates.

The polymerisation phenomena of the higher sesquioxide silicates are more difficult. The sesquioxide disilicate, $R_2O_3 \cdot 2SiO_2$, may possibly have the symmetrical formula

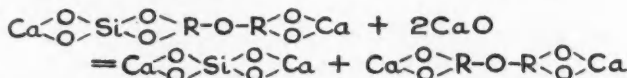


The corresponding tri-, tetra- and hexa-silica compounds may be given a silica chain structure. The fact that the decomposition of their calcium compounds proceeds with the formation of $CaO \cdot SiO_2$ shows that the SiO_2 is not very stably combined, and the following formulæ may be applied,



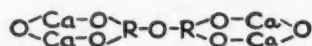
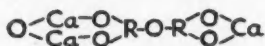
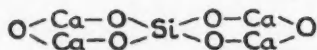
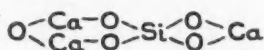
The silica chain is further extended for the compounds $R_2O_3 \cdot 4SiO_2$ and $R_2O_3 \cdot 6SiO_2$.

The presence of these silica chains renders plausible the ready breaking of the chains in the constituents of cement raw material in the presence of free lime. The molecules are thus broken down with the formation of $CaO \cdot SiO_2$ until the compound $R_2O_3 \cdot SiO_2$ is reached. If the amount of free lime is further increased the $R_2O_3 \cdot SiO_2$ is finally broken down with the formation of separate calcium silicate and aluminate.



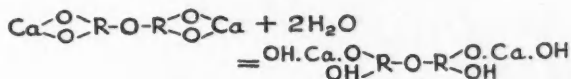
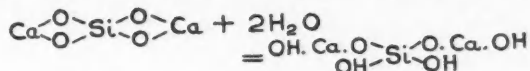
The decomposition of the compounds in the raw materials can be regarded as complete with the formation of $2CaO \cdot R_2O_3 \cdot SiO_2$, and the formation of the separate calcium silicate and aluminate represents the actual formation of cement substance. The hydraulic properties of cement are due to compounds of the types $2CaO \cdot SiO_2$ and $2CaO \cdot Al_2O_3$, and to compounds of still higher lime content such as $3CaO \cdot SiO_2$, the existence of which has been definitely proved.

In the two dicalcium compounds all the normal valencies are fully saturated and higher lime compounds can only be represented by polymerisation chains. The following are thus obtained:

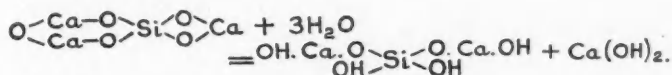


The compound $3\text{CaO} \cdot \text{SiO}_2$ is, of course, known. $4\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{R}_2\text{O}_3$ and $4\text{CaO} \cdot \text{R}_2\text{O}_3$ are obviously theoretically possible, and research into the possibilities of preparing them should be well repaid, since they are analogous to $3\text{CaO} \cdot \text{SiO}_2$ and should split off free lime on hydration and possess the properties of extremely active cements.

The hydration of the disilicates and aluminates (or ferrites) proceeds with the simple addition of water without altering the molecular skeleton.



The compounds of higher lime content are hydrated similarly, with the simultaneous formation of free Ca(OH)_2 .



Similarly for $4\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{R}_2\text{O}_3$ and $4\text{CaO}.\text{R}_2\text{O}_3$.

Not only do the compounds formed by the addition of water possess hydraulic properties, but the free $\text{Ca}(\text{OH})_2$ formed is able to combine with SiO_2 to give $2\text{CaO} \cdot \text{SiO}_2$, which also possesses hydraulic properties. The hydraulic properties of a cement are thus improved by increasing the amount of lime in the molecule which can be set free in this way. Let the hydraulic strength of a molecule of CaO be taken as unity, then 100 parts by weight will correspond to a strength factor 1.8. One hundred parts of $2\text{CaO} \cdot \text{SiO}_2$ (molecular weight 172) will correspond to strength factor $100 \times \frac{2}{172} = 1.16$ and 100 parts $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ to

$100 \times \frac{2}{214} = 0.93$. Similar factors for other silicates and aluminates are $3\text{CaO} \cdot \text{SiO}_2 = 1.32$, $4\text{CaO} \cdot \text{SiO}_2 = 1.40$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = 1.11$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 = 1.23$.

The production of cement can be described by the equation



The purpose of making cement is to fix the energy introduced so that it can be again set free as easily as possible when required. The energy is fixed in the lime, which reproduces it as hydraulic strength on hydration. The higher the lime content the greater must be the energy held by the cement and the hydraulic strength, as is shown by the hydraulic strength factors given. From these it would appear that pure lime must have the highest hydraulic strength factor, and that lime mortars should give greater mechanical strength, *i.e.*, higher hydraulic power, than the best cements. This at first sight seems absurd. The

masonry of antiquity shows, however, that lime mortars can attain great mechanical strength; such structures, built with lime prepared in a very primitive way, often compare favourably with modern work. It is impossible as yet to say what strengths would be attained ultimately by modern cements since the cement industry is only a hundred years old, and the older empirical cements do not provide a fair basis of comparison. It is within the bounds of possibility that although cement at first increases in strength more rapidly than lime mortar, the ultimate strength of lime may be the greater. That increase in lime content is definitely related to increased strength is proved by modern high-lime, high-strength cements—better termed high-early-strength cements.

It must not be forgotten that there are two stages in the setting process. The first is the internal hydration of the calcium silicates, aluminates, and ferrites, a process which takes place within the cement grains. This is probably related to the so-called initial strength. This internal hydration is rapidly completed, since the necessary molecular structure is already present and the water can immediately combine with it. The second stage is the external hydration, *i.e.*, the hydration of the silicates corresponding to the liberated lime. Since there is no further silica available in the cement grains, the freed lime must seek out and combine with the silica of the materials added to the cement. The completion of this external hydration corresponds to the ultimate strength.

Just as the initial strength has been increased by careful choice of materials, preliminary grinding, mixing, burning and clinker grinding, to the degree given by modern high-early-strength cements, so must future development proceed in the direction of accelerating the attainment of the ultimate strength. The way to this goal has already been unknowingly trodden. It is well known that the presence of free lime in cement renders it susceptible to the attack of acids and salt solutions, and that high-strength cement—with its higher lime content—is more readily attacked than ordinary Portland. The latter is in its turn more easily attacked than blast-furnace cement, with its still lower lime content. Further, it is possible still more to reduce the susceptibility of cement to attack by the addition of chemically active silica.

Such additions, previously only used from the point of view of protection against acids, are also destined to solve the problem of the attainment of ultimate strength, since by this means the free lime can be brought into combination with silica. At present the only objective is the combination of the free lime as $\text{CaO} \cdot \text{SiO}_2$. Future work must attempt to produce $2\text{CaO} \cdot \text{SiO}_2$ in the cement by combination of the free CaO and active SiO_2 with the objects of improving resistance to acids and accelerating the attainment of ultimate strength. Success in this direction—towards which trass cement is perhaps the first step—would be of great interest to the cement industry and would bring lime to a position of importance once more. It would possibly revolutionise the present conception of cement, replacing modern cements by a composition of lime containing the highest possible content of highly-active silica. The ultimate strength of such lime-silica mortars might even exceed that of the best present-day cements.

New Cement Plant in Southern Europe.

OUR illustrations relate to a cement plant, operating on the wet process, recently erected in the south of Europe. The works has a capacity of 225 tons a day, and arrangements have been made in designing the plant for doubling its output, should this be required at a later date, without stopping production.

The raw materials used are hard crystalline limestone and plastic clay, which undergo primary reduction in a hammer mill and reach the plant via a trough conveyor. For the handling within the works of the primary-crushed raw materials, the clinker and the coal before it is pulverised, a travelling crane with grab is employed. Owing to the use of the crane the plant falls into two longitudinal divisions (Fig. 1), one-half of the building accommodating the mechanical equipment, i.e., the mills, the rotary kiln, and the coal pulverising plant, and the other portion containing storage spaces for raw materials, clinker, gypsum and raw coal which are handled by the crane.

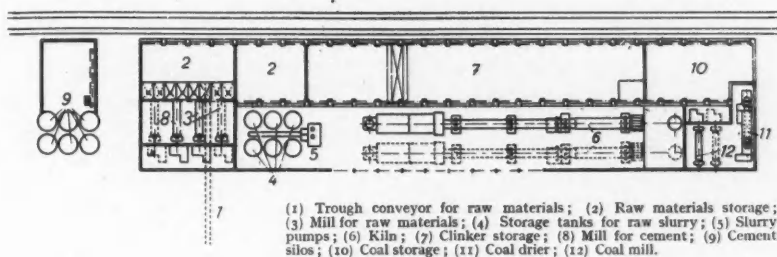


Fig. 1.

The raw materials are ground in a three-compartment compound mill, 7 ft. 3 in. in diameter and 39 ft. 4 in. long, which is equipped, as are also the cement and coal mills, with the patented Krupp "Centra" drive, and is fed by two rotary plate feeders. The capacity of the wet mill is about 25 tons per hour with 6 to 8 per cent. residue on the 180 x 180 sieve, calculated upon dry material. The slurry is dealt with throughout the plant by centrifugal pumps of special design. By the use of highly wear-resistant materials for the impeller and guide wheel of the pump, the machines work for months on end without causing trouble. For the raw slurry six storage tanks are provided, a compressor supplying the compressed air needed for mixing purposes. In addition to six mixing nozzles each slurry tank is equipped with a "Mammut" pump for intimately mixing the raw materials.

The "Concentra" kiln, 9 to 11 ft. in diameter and 210 ft. in length (Fig. 2), has 13 cooling cylinders and is fitted with a patented arrangement of chains in

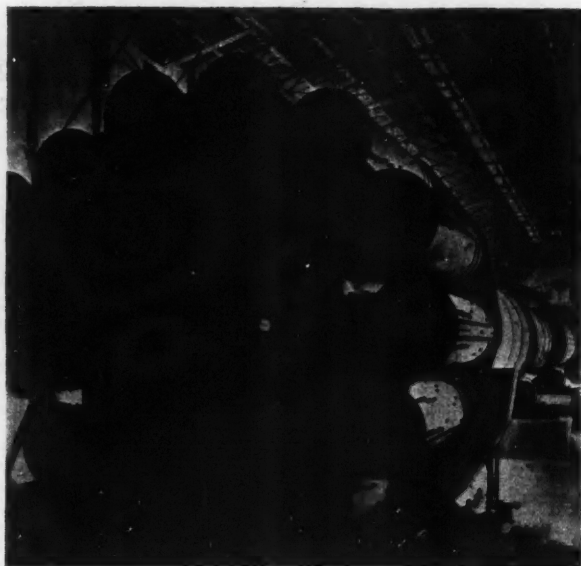


Fig. 2.

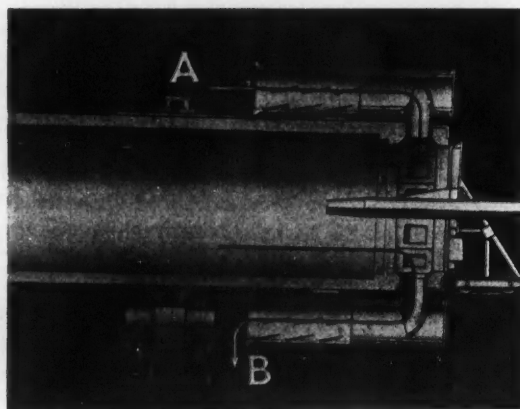


Fig. 3.

the preheating zone. Without special devices following the kiln, this provision permits the attainment in continuous service of an exit gas temperature of about 392 deg. F. Losses via flue gases, radiation and clinker waste heat are small, and thermal efficiency is achieved without special equipment.

The arrangement of the cooling cylinders and the method of support result in low headroom requirements. By subdivision of the cooler, separate small cooling chambers are formed, so that the combustion air flowing to the kiln through the cooling cylinders comes into such effective contact with the hot clinker that the latter is efficiently cooled and the combustion air enters the kiln at a high temperature. Another source of increased cooling effect lies in the fact

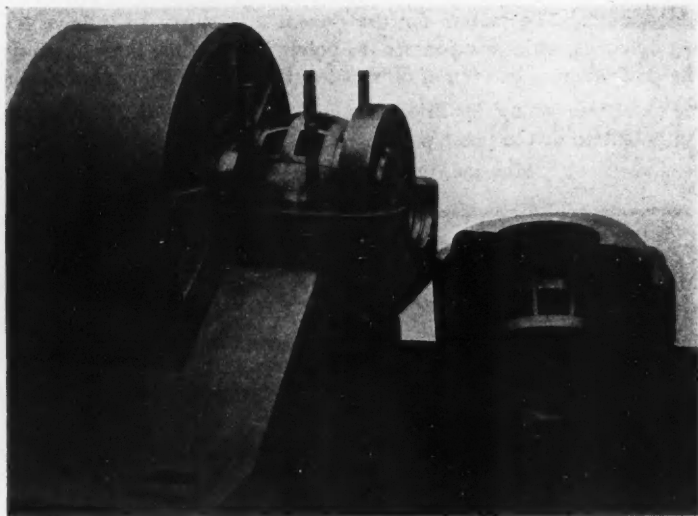


Fig. 4.—Rotary Kiln Bearing.

that the clinker travels in the cooling cylinders in the opposite direction to its progress in the kiln, and hence is exposed to the cooling air for a long period. Fig. 3 shows the path of the cooling air (A) and the clinker (B) in the kiln and in the cooling cylinders. The temperature of the clinker on leaving the cooler, with a daily kiln output of approximately 200 tons, is about 212 deg. F.

The cooling cylinders are protected from wear and radiation losses are minimised by a lining provided with strong scoops for lifting and dropping the clinker. At the points where the clinker leaves the kiln for the coolers, the clinker is spread out by cooling pieces fitted in the kiln and undergoes preliminary cooling. These

cooling pieces are made of special Krupp heat-resisting steel, which retains great hardness even at high temperatures. Of the total combustion air, 90 per cent. passes through the cooling cylinders.

We are informed that no damage to the chains in the kiln has resulted from contact with hot flue gases under conditions of continuous operation, the chains in the preheating zone preventing the plastic raw material from forming slurry rings.

The coal for firing the kiln is dried in a drying drum heated by powdered coal and then pulverised in a compound mill, 5 ft. 3 in. in diameter and 26 ft. 3 in. in length, to give a residue of about 10 per cent. on the 180 \times 180 sieve.

Practically all machines are furnished with individual electric motor drive and directly coupled. Where necessary, geared motors and variable speed motors have been used. The motors for the cement and slurry mills have built-on exciting dynamos, which compensate the power factor of the three-phase system. For the production of one ton of cement less than 90 kW.-hours are required.

The plant was erected by Fried. Krupp Grusonwerk A.-G., Magdeburg, who are the patentees of the plant used.

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